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PATENT SPECIFICATION

(11) 1 503 333

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(21) Application No. 50285/75 (22) Filed 8 Dec. 1975

(31) Convention Application No. 49/142158

(32) Filed 10 Dec. 1974 in

(33) Japan (JP)

(44) Complete Specification published 8 March 1978

(51) INT CL² D06P 5/00

(52) Index at acceptance

D1B 2C1A1 2C1A2 2C1A5 2C1A6 2C1A7 2C1A8 2C2B 2C2D1B 2C2F 2C2K 2C2M 2L1B 2L2A 2L3 2L5A 2L5D1 2L5D2 2L5D 2L6 2L9 2S

(19) THE PATENT OFFICE LONDON

(54) PROCESS FOR PATTERNWISE DYEING OF TEXTILE FABRICS

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process of dyeing textile fabrics. More specifically, it relates to a process of dyeing textile fabrics in print patterns by utilizing microcapsules containing a dye solution, to transfer sheets which can be used in such process and to the fabric thus dyed.

For carrying out textile printing, a sublimation transfer method has previously gained wide acceptance (see, for example, Japanese Patent Publications Laid-Open 19169/74, 87881/74, 94409/74 and 104711/74). This method comprises printing a print pattern with a sublimable dye onto a base material which has been subject to a special treatment (for example, undercoating) to form a transfer sheet, superimposing the transfer sheet on a textile fabric, and heating the transfer sheet to transfer the pattern onto the fabric. This method enables the print pattern to be transferred with simplicity, but suffers from the defects that the print pattern can be transferred only to fabrics of synthetic fibers which have a glass transition point, and the dyes that can be used are limited to sublimable dyes.

In an attempt to remove such defects, textile printing methods using microcapsules have recently been extensively investigated. These methods involve printing microcapsules containing a dye solution onto a sheet to form a transfer sheet, superimposing the transfer sheet on a textile fabric, and transferring the dye solution in the microcapsules to the fabric by breaking the microcapsules by pressure or heat, or by the action of a solvent, to thereby dye the fabric. By such method, however, the transfer of the dye solution to the fabric does not result in complete fixing of the dye onto the fabric, the density of the dyed prints is not sufficient, or the dye bleeds out upon washing, fades out under sunlight, or discolors upon exposure to the air. It is necessary, therefore, to treat the dyed fabric to increase its fastness properties. Specifically, this is done by dipping the dyed fabric in a treating liquor containing a fastness improver so as to fix the dye. For this reason, these methods cannot be operated as a complete dry process, and have the defect that when the dyed fabric before dye fixing is dipped in a dye fixing bath, the unfixed dye diffuses and the print pattern becomes blurry.

It is an object of this invention therefore to provide a textile printing process using microcapsules containing a dye solution and different microcapsules containing a solution of a fastness improver, which can be practiced as a completely dry process.

Another object of this invention is to obtain dyeings free from dye bleed-out and having superior fastness properties.

The process of the invention comprises applying microcapsules containing a solution of a dye and microcapsules containing a solution of a fastness-improving agent onto a textile fabric in a print pattern, either directly or through a transfer sheet, and releasing the dye solution and the fastness-improver solution from the microcapsules onto the fabric to thereby dye the fabric and improve the fastness properties of the dyed fabric.

The process of this invention can be performed in accordance with various embodiments, which are shown below.

(1) A method which comprises printing microcapsules containing a dye solution and microcapsules containing a solution of a fastness-improver onto a sheet in a pattern, superimposing the resulting transfer sheet onto a textile fabric, and subjecting the transfer sheet to pressure, heat or solvent action to thereby release the dye solution and the fastness improver solution onto the textile fabric.

(2) A method which comprises coating or printing one of (a) microcapsules containing

a dye solution or (b) microcapsules containing a fastness-improver solution onto a transfer sheet and the other of (a) or (b) onto a textile fabric, superimposing the transfer sheet onto the textile fabric and thereafter rupturing the microcapsules as described above to complete the dyeing.

(3) A method which comprises printing both microcapsules containing a dye solution and microcapsules containing a fastness-improver solution onto a textile fabric, and subjecting the textile fabric to pressure, heat or solvent action to thereby complete the dyeing.

(4) A method which comprises applying microcapsules containing a dye solution onto a textile fabric, breaking the microcapsules to dye the fabric, then superimposing a sheet coated with microcapsules containing a fastness-improver solution onto the dyed fabric, and subjecting the assembly to a fixing treatment such as pressure or heat to thereby fix the dye. This method is especially advantageous for obtaining multi-colored prints. For example, when red, blue and yellow prints are formed using microcapsules containing dyes of these colors and then treated with microcapsules containing a solution of a fastness-improver, a multi-colored print of high fastness can be obtained.

(5) A method which comprises coating both microcapsules containing a dye solution and microcapsules containing a solution of a fastness-improver onto a transfer sheet, superimposing the transfer sheet onto a textile fabric and breaking these microcapsules by the pressure of a roll having the desired pattern surface engraved thereon to thereby dye and fix the fabric in the engraved pattern.

(6) A method which comprises coating microcapsules containing a dye solution and microcapsules containing a solution of a fastness-improver onto a sheet, and interposing a sheet (e.g., a plastics sheet) having pores provided in the desired pattern between the coated sheet and a textile fabric to thereby break the microcapsules and dye the fabric in the pattern.

(7) A method which comprises applying microcapsules containing solution of dyes of different colors onto a textile fabric, rupturing the microcapsules to thereby form multi-colored prints on the fabric, then superimposing a sheet coated with microcapsules containing at least one fastness improving agent onto the fabric, and then rupturing the microcapsules containing at least one fastness-improving agent to thereby fix the dyes.

In the process of this invention, the transfer is carried out preferably at a temperature of 20 to 250°C and a pressure of 10 to 800 kg/cm^2.

The dyes and fastness-improving agents suitable for use in the process of this invention include all those which are generally used in the field of dyeing textile fabrics.

The dyes can be either oil-soluble or water-soluble, and are selected, for example, from acid dyes, mordant dyes, basic dyes, disperse dyes, direct dyes, sulfide dyes, vat dyes, azoic dyes and reactive dyes. Specific examples of these dyes are given, for instance, in the Japanese publication, *Lectures in Dyeing Treatment*, Vol. 1 to Vol. 13 (published by Kyoritsu Shuppan Co., Ltd., Tokyo) and Maedo, *Dyeing and Finishing of Chemical Fibers*, (1969), published by Chijin Shokan, Tokyo).

The fastness-improver has the effect of (a) precipitating the dye, (b) reacting with the dye to render it insoluble or (c) forming a covalent bond between the reactive groups of the dye and the reactive groups of the fibers to thereby fix the dye to the fibers. It increases the dye exhaustion, improves the fastness of the dyed fabric to rinsing, or reacts with the reactive groups of the dye to stabilize them and thereby prevent discoloration and improve light fastness.

There is no limitation on the types of fibers which can be dyed in accordance with the present invention, i.e., it can be applied to all conventionally dyed fibers. Examples of fibers are natural fibers such as cotton, wool or silk, and synthetic fibers such as polyacrylonitrile, nylon, polyester or mixtures thereof.

Specific examples of the fastness-improver are metal salts (for example, alkali metal salts such as sodium acetate, potassium bichromate, sodium sulfite, sodium sulfate, sodium nitrate or a sodium compound of neutral copper tartrate; chromium salts; chromic acid salts; aluminum salts; iron salts; tin salts; copper salts; or calcium salts), ammonium salts (such as ammonium sulfate or ammonium acetate), acids (such as sulfuric acid, formic acid, acetic acid or hydrochloric acid), alkalies (such as sodium carbonate, sodium bicarbonate or sodium silicate), diazo compounds, aldehydes (such as formaldehyde, glyoxal or glutaraldehyde), and cationic surface active agents such as triethylbenzyl ammonium chloride, lauryl pyridinium chloride.

Some examples of especially useful combinations of dyes and fastness improvers are as follows:

Dyes	Fastness Improver
Direct dyes	Metal salts
Acid dyes	Acids
Basic dyes	Metal salts, acids
Mordant dyes	Metal salts, ammonium salts
Reactive dyes	Alkalies

Microencapsulation of the dyes and fastness improver can be performed by any conventional method known in the pharmaceutical, dye, copying paper or photographic field. Specific microencapsulating methods disclosed, for example, in U.S. Patents 2,800,457, 2,800,458,

3,287,154, 3,429,827, 3,432,327, 3,796,669 and 3,818,250, British Patents 990,443 and 1,091,076, and French Patent 1,362,933, can be used.

The concentration of the dye in the microencapsulated dye solution is usually 0.1 to 50% by weight, preferably 1 to 30% by weight, and the concentration of the fastness improver in the microencapsulated solution is usually 0.5 to 60% by weight, preferably 1 to 50% by weight. The coating weight ratio of dye microcapsules to the fastness-improver microcapsules is most preferably 0.025 to 40 on a commercial scale. Desirably, the microcapsules have a size of 20 to 200 microns. The solvent used for dissolving the dye or the fastness-improver to be microencapsulated may be any aqueous or oily liquid which dissolves the dye or the fastness improver (water, or a water-miscible or water-immiscible liquid), e.g., dibutyl phthalate, amyl acetate, dibutyl maleate.

The resulting microcapsule liquids which are applied are dispersions having a solids content of 1 to 50% by weight. When such a dispersion is coated on a base material (e.g., paper, a plastic sheet, or a metal sheet) in an amount of 0.5 to 20 g/m^2 followed, if desired, by drying, a transfer sheet can be obtained. If required, a binder can be added to the microcapsular dispersion. Examples of the binder are water-soluble polymeric substances (for example, natural substances such as starch or shellac or a synthetic substance such as methyl cellulose, polyacrylamide, polyvinyl alcohol or carboxymethyl cellulose), and oil-soluble polymeric substances (such as nitrocellulose or ethyl cellulose).

According to the process of this invention, microcapsules containing a solution of a dye and/or microcapsules containing a solution of a fastness-improver can be printed by known printing methods (for example, silk-screen printing or gravure printing techniques) onto a textile fabric composed of synthetic fibers such as polyamide, polyacrylic or polyester fibers, natural animal or vegetable fibers such as cotton, wool or silk, or blends of these fibers either directly or through a transfer sheet.

The dye solution and the fastness-improver solution are included in separate microcapsules, and in application, are released onto the fabric. Thus, no precipitation or degeneration of the dye occurs. In addition, the dyeing operation is simple, and since no rinsing is required, the process does not yield waste water which causes environmental pollution.

The following Examples illustrate the present invention.

EXAMPLE 1

2 g of Sumifix Brilliant Blue R (trademark for a reactive dye-Reactive Blue-19, a product of Sumitomo Chemical Co., Ltd.) was dissolved in 10 g water, and 20 g of glycerin was added to the solution to form a dye solution (solution A). Separately, 6 g of Coronate-L (trademark for a 3:1 (mol ratio) adduct of tolylene diisocyanate and trimethylol propane, a product of Nippon Polyurethane Co., Ltd.) was dissolved in 100 g of toluene to form a solution (solution B). With vigorous stirring, solution A was emulsified in solution B to form liquid droplets with a diameter of 40 microns at 25°C. The above procedure was carried out at room temperature. With gentle stirring, the emulsion containing the liquid droplets was heated up to 40°C and stirred at this temperature to complete microencapsulation. The above procedure afforded microcapsules enclosing the dye solution in a shell of the Coronate-L polymer.

4 g of sodium carbonate as a fastness-improver was dissolved in a mixture of 10 g of water and 20 g of glycerin to form a dye improver solution (solution C). Solution C was treated in the same way as in the case of solution A to form microcapsules containing the fastness-improver solution in a shell of the Coronate-L polymer.

The total amount of microcapsules containing the dye solution thus prepared was mixed with the total amount of the microcapsules containing the fastness-improver solution thus prepared (in both instances there was substantially complete use of the wall forming components in the coacervation), and 12 g of nitrocellulose (m.w. ca. 3,000) as a binder was added to the resulting microcapsular dispersion. Furthermore, 60 g of ethyl acetate was added to dissolve the nitrocellulose and thus to prepare a printing ink. The printing ink was printed on a sheet of paper by gravure coating to form a transfer sheet. The transfer sheet was superimposed on a cotton fabric, and placed under a pressure of 100 kg/cm^2 to thereby dye a blue mark on the cotton fabric. Even when the dyed fabric was washed for 10 minutes with water at 20°C, the density of the dyed mark was not reduced, nor was the mark discolored.

For comparison, a printing ink was prepared in the same way as above except that the microcapsules containing the fastness-improver solution were not used. The printing ink was coated in the same way as above to form a transfer sheet, and a mark was printed on a cotton fabric using the transfer sheet. The dyed mark substantially disappeared upon washing with water, and only traces thereof remained. It was also found that when sodium carbonate was added to solution A, the dye precipitated and microencapsulaaiton did not proceed sufficiently.

EXAMPLE 2

The microcapsules containing the dye solution as obtained in Example 1 were mixed with the microcapsules containing the fastness-improver solution as obtained in Example 1,

and 30 g of ethyl cellulose as a binder was added to the mixture. Further 50 g of ethyl acetate was added to dissolve the ethyl cellulose.

The microcapsular dispersion was coated on a polyethylene sheet, which had been subjected to a conventional corona discharge treatment to improve wettability and adhesiveness of the polyethylene surface to the coating solution, to form a transfer sheet. The transfer sheet was superimposed on a cotton fabric, and pressed by a roller (40°C; 400 kg/cm^2) having a pattern-engraved surface. A dyed mark was formed in the pattern on the cotton fabric. The mark did not discolor or fade upon washing with water, and exhibited superior fastness properties.

EXAMPLE 3

Microcapsules containing a dye solution were prepared in the same way as in Example 1 except that 4 g of Suminol Fast Red G (trademark for an acid dye-Acid Red-118, a product of Sumitomo Chemical Co., Ltd.) was used instead of 2 g of the Sumifix Brilliant Blue R used in Example 1. Furthermore, microcapsules containing a fastness-improver solution were prepared in the same way as in Example 1 except that 3 g of an 80% aqueous solution of acetic acid was used instead of 4 g of sodium carbonate as the fastness-improver. The microcapsules containing the dye solution were mixed with the microcapsules containing the fastness-improver solution as in Example 1, and a solution of 20 g of ethyl cellulose in 60 g of ethyl acetate was added to the mixture to form a printing ink.

The printing ink was applied in a pattern to a sheet of paper, which had been surface-coated with a polyurethane resin, by a silk-screen printing method to form a transfer sheet. The transfer sheet was superimposed on a wool fabric, and pressed to form a red dyed mark on the fabric. The mark did not discolor upon washing with water or extraction with a petroleum-type solvent, and exhibited superior fastness properties.

WHAT WE CLAIM IS:—

1. A process of printing a textile fabric in a print pattern, which comprises patternwise applying microcapsules containing a solution of at least one dye and microcapsules containing a solution of at least one fastness-improving agent for the dye to a textile fabric, either directly or by transfer from a transfer sheet, and releasing the dye solution and the fastness-improver solution from the microcapsules onto the fabric to thereby fast dye the fabric.

2. A process as claimed in Claim 1, wherein the release of the solutions is effected by rupturing the microcapsules at a temperature of 20°C to 250°C and a pressure of 10 to 800 kg/cm^2.

3. A process as claimed in Claim 2, wherein the dye is selected from acid dyes, mordant dyes, basic dyes, disperse dyes, direct dyes, vat dyes, sulphide dyes, azoic dyes and reactive dyes.

4. A process as claimed in Claim 1, 2 or 3, wherein the fastness-improving agent is selected from metal salts, acids, ammonium salts, alkalies, diazo compounds, aldehydes and cationic surface active agents.

5. A process as claimed in Claim 1 or 2, wherein the dye is a direct dye and the fastness-improving agent is a metal salt.

6. A process as claimed in Claim 1 or 2, wherein the dye is an acid dye and the fastness-improving agent is an acid.

7. A process as claimed in Claim 1 or 2, wherein the dye is a basic dye and the fastness-improving agent is a metal salt or an acid.

8. A process as claimed in Claim 1 or 2, wherein the dye is a mordant dye and the fastness-improving agent is a metal salt or an ammonium salt.

9. A process as claimed in Claim 1 or 2, wherein the dye is a reactive dye and the fastness-improving agent is an alkali.

10. A process as claimed in any preceding claim, wherein the microcapsules have a size of 20 to 200 microns.

11. A process as claimed in any preceding claim, wherein the concentration of the dye in its solution is 0.1 to 50% by weight.

12. A process as claimed in any preceding claim, wherein the concentration of the fastness-improving agent in its solution is 0.5 to 60% by weight.

13. A process as claimed in any preceding claim, wherein a binder for the microcapsules is added to the microcapsules prior to the application thereof to the fabric.

14. A process as claimed in any preceding claim, wherein the textile fabric is a woven fabric made of synthetic, natural vegetable or animal fibres, or a blend of these fibres.

15. A process as claimed in Claim 1 of printing a textile fabric, substantially as hereinbefore described in any of the Examples apart from the comparison portions thereof.

16. A transfer sheet for printing textile fabrics in print patterns comprising a support coated with microcapsules containing a fastness-improver for the dye.

17. A transfer sheet as claimed in Claim 16, wherein the microcapsules or their contents are as defined in any of Claims 2 to 12.

18. Fabric printed by the process of any of Claims 1 to 15.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa. 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.